Composition and origin of the aliphatic extractable hydrocarbons in the Puertollano (Spain) oil shale

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Abstract—The composition of the saturated aliphatic fraction extractable from the Puertollano oil shale, the most important deposit of this material in the Iberian Peninsula, has been studied by GC and GC–MS. This fraction contained mainly *n*-alkanes, *n*-alkylcyclohexanes, and *n*-alkylmethylcyclohexanes. The cyclohexanes showed a distribution very similar to that of *n*-alkanes suggesting a common origin. Contributions from higher plant derived material (mainly conifers) were apparent, based on the presence of diterpenoid compounds. An angiosperm contribution was evidenced by the presence of *des*-A-triterpenoid hydrocarbons, derived from oleanane and ursane skeletons. Hopanes, 8,14-*seco*hopanes, ring-D aromatized 8,14-*seco*hopanes, benzohopanes, a C_{24} 17,21-*seco*hopane and a C_{31} hexacyclic saturated hopane were found in the extracts, showing the influence of microorganisms. Different pathways are suggested for the formation of benzohopanes, and the C_{31} hexacyclic hopanoid found in the extracts.

Key words—Puertollano oil shale, biomarkers, 8,14-*seco*hopanes, benzohopanes, terpanes, steranes

INTRODUCTION

The oil shale from Puertollano is the most important deposit of this type in the Iberian Peninsula. It forms part of a virtually undeformed intramontane basin of Late Stephanian age in the Southern part of La Mancha (Central Spain) and contains both bituminous shales, and high volatile bituminous coals, in a generally lacustrine succession. Details on the geological settings of this deposit have been described by Wagner (1985). Seam B in the Calvo Sotelo Oil Shale Mine was the most important one commercially and was exploited for obtaining mineral oil by distillation during several decades; it was abandoned for economic reasons in 1964. Substantial reserves of oil shale remain, and these may become economic again when oil prices rise.

Despite intensive exploration activity in the Puertollano Basin, few geochemical studies have been reported in the literature. The first organic-geochemical studies of this deposit were exclusively centered on the physico-chemical characterization of the kerogen fraction (Robinson and Dineen, 1967; Robinson, 1969). A partial biomarker description, and some petrographic analysis of the Seam B of the Puertollano oil shale deposit, have recently been reported (Kruge and Suarez-Ruiz, 1991; Borrego *et al.*, 1992; Blanco *et al.*, 1992).

To achieve an organic-geochemical characterization of the Puertollano oil shale (POS) from an integrated point of view we are carrying out several studies. They include an inventory of aliphatic, aromatic and functionalized biomarkers, and the characterization of the kerogen by degradative and spectroscopic methods. This paper presents a study, by GC–MS, of aliphatic hydrocarbons in order to determine their origin and geochemical significance. Preliminary data on the composition and organic-geochemical significance of the aromatic fraction, and the kerogen, have already been described (Martín *et al.*, 1991; del Río *et al.*, 1993).

MATERIALS AND METHODS

The composite log of the stratigraphic succession in the Puertollano coal and oil shale field has been already described in Wagner (1985). Figure 1 shows the locale map of the Puertollano Basin in the Iberian Peninsula, and Fig. 2 shows the stratigraphic section of the lower part of the Puertollano succession as exposed in the (now abandoned) Calvo Sotelo Oil Shale Mine, in the central part of the Puertollano coal and oil shale field (around 400 m subsurface). Mainly tuffaceous mudstones, one sandstone and two thin tuff bands have been found below the second oil shale horizon (Seam B) which is the one worked in the past by the Calvo Sotelo Mine (Fig. 2). Several thin tuff bands in this oil shale horizon apparently confirm the association with volcanic emissions. Well preserved fish remains occur in these bituminous shales, and particularly in the top part (Forey and Young, 1985). Drifted plant remains include conifer branches. Table 1 shows some important geochemical characteristics of the sample taken from the POS (Seam B) selected for this study.

The ground and sieved sample (50 g) was exhaustively Soxhlet-extracted with toluene/methanol (3/1). The successive extracts were combined, and dried under reduced pressure. The extractable organic matter (EOM) was 9.6 mg/g rock. After removal of the asphaltenes by precipitation with *n*-pentane, the total saturated hydrocarbon fraction (with some monoaromatics) was isolated by adsorption chromatography on a column (20 × 1 cm) of Florisil eluting exhaustively with *n*-hexane. The saturated fraction (3.1 mg sat./g rock) was further enriched in branched and cyclics by removing the *n*-alkanes with 5 A molecular sieve.

GC and GC–MS chromatographic analyses were carried out on Hewlett–Packard systems 5730A and 5988A respectively using fused silica capillary columns (25 m) coated with OV-101. N_2 (GC) and He (GC–MS) at rates of 1 ml/min were used as carrier gases. The samples were injected in the splitless mode (1/60 split ratio and 2 ml/min septum purge) with a multiramp heating program: from 50 to 100°C at 32°C/min, and from 100 to 300°C at 6°C/min. The injector and detector were set at 300°C. The identity of the compounds was determined by comparison of their mass spectra with those tabulated (EPA/NIH Mass Spectral Data Base), stored in computer libraries (NBS, Wiley) or previously published. Some homologous series were detected by single or multiple monitoring of diagnostic ions (SIM, MID). Quantitation of hydrocarbons was by peak area integration in the GC-FID traces using an external standard containing *n*-tetradecane, *n*-docosane and cholestane.

RESULTS AND DISCUSSION

Table 2 shows the different series of compounds detected in the saturated fraction of the POS, with an indication of the predominant components, and their relative abundances. The structures of each type of compounds (in Roman numbers throughout the text) are shown in the Appendix.

Alkanes and alkylcyclohexanes

The hydrocarbon fraction was characterized by a series of *n*-alkanes in the range C_{13}–C_{35} as shown in Fig. 3. This series exhibited a very slight odd-over-even predominance, a maximum at C_{25} and a pre-

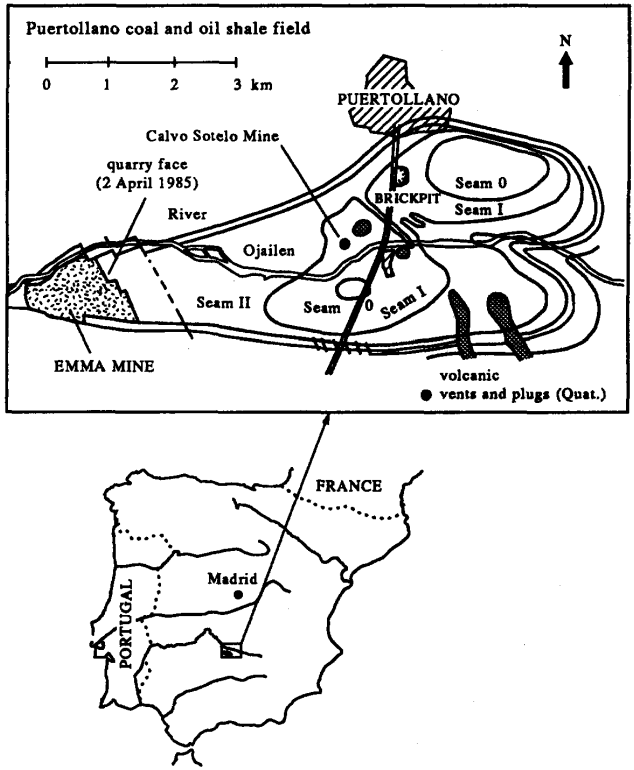

Fig. 1. Location map of the Puertollano Basin in the Iberian Peninsula, and position of the Calvo Sotelo Mine in the Puertollano coal- and oil-shale field.

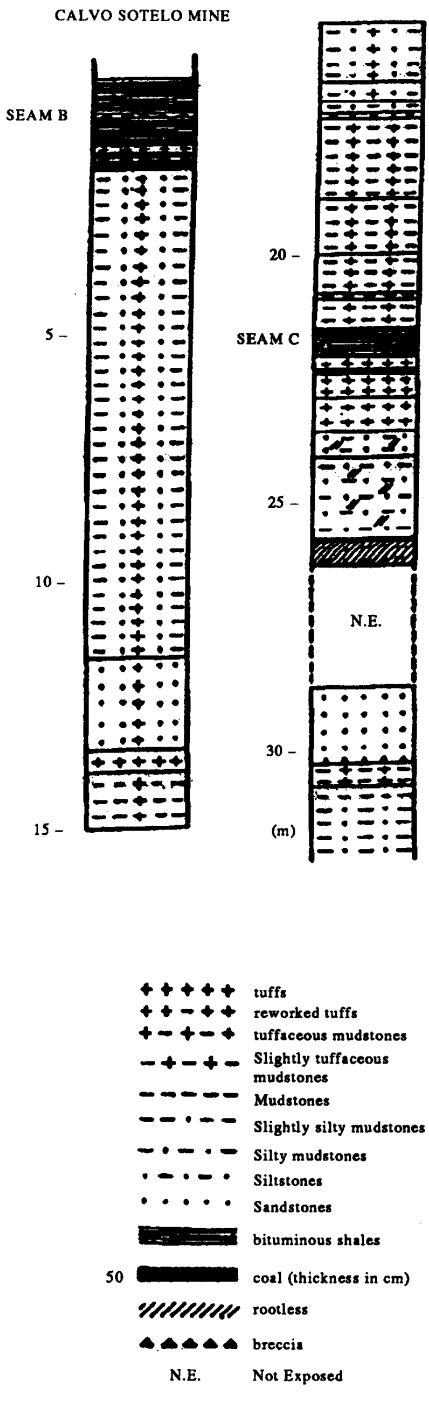

Fig. 2. Stratigraphic succession of the lower part of the Puertollano Basin at the Calvo Sotelo Mine.

dominance of the $>C_{23}$ homologs. Although the uniform *n*-alkane distribution does not allow a clear differentiation of different inputs, the lower homologs are interpreted to be derived from bacterial and/or algal debris whereas the biological sources for *n*-alkanes $>C_{23}$, with the slight odd carbon number predominance, can be attributed to terrestrial plant waxes and/or algal lipids (Simoneit, 1978). Aliphatic acyclic isoprenoids, mainly phytane (C_{20}), pristane (C_{19}), norpristane (C_{18}) and farnesane (C_{15}) were also encountered with a Pr/Ph ratio of 2.8.

Series of *n*-alkylcyclohexanes (C_{13}–C_{28}) (**I**, Appendix 1) and *n*-alkylmethylcyclohexanes (C_{18}–C_{28}) (**II**) were also found in the branched/cyclic fraction by monitoring the ions at *m/z* 83 and 97 respectively. Three different isomers, with methyl group in *ortho*-, *meta*- and *para*-positions were detected for the *n*-alkylmethylcyclohexane series. The distribution of the alkylcyclohexanes in the POS (shown in Fig. 4) is similar to that of the *n*-alkanes. This suggests a diagenetic relationship between the alkylcyclohexanes and the *n*-alkanes (or their likely precursors, the *n*-fatty acids). Ring closure of either the *n*-paraffins, or their precursors (e.g. fatty acids), has been suggested by several authors (Rubinstein and Strausz, 1979; Fowler *et al.*, 1986).

Terpenoid and steroid hydrocarbons

Among the polycyclic hydrocarbons identified in the POS extracts were sesqui-, di- and triterpenoid and steroid hydrocarbons.

The partial chromatogram (Fig. 5) shows the trace of *m/z* 123, which corresponds to the series of bicyclic sesquiterpanes (C_{14}–C_{16}) detected in the extracts. The different structures were determined by comparison of their mass spectra with those previously reported (Alexander *et al.*, 1984; Philp, 1985; Weston *et al.*, 1989). The predominant homologues were 8β(H)-drimane (**III**, R = CH_3) and 8β(H)-homodrimane (**III**, R = C_2H_5) with small amounts of other isomers. Alexander *et al.* (1984), suggested that drimane type compounds are probably formed by biological alteration of hopanoid precursors during diagenesis. In fact, the 8β(H)-drimane and 8β(H)-homodrimane have both structural and steric similarities to the A/B

Table 1. Some geochemical parameters of the Puertollano oil shale

Proximate analysis (%)	
Moisture	0.64
Volatiles	19.75
Fixed carbon	8.85
Ash	70.76
*Elemental analysis** (%)	
C	70.25
H	8.98
N	1.85
S	4.30
O†	14.62
Vitrinite reflectance (%)	0.40
Extractable organic matter (mg/g rock)	9.60
Saturates (mg/g rock)	3.10

*Dry, ash-free.
†By difference.

Table 2. Main series of compounds detected in the saturated fraction of extracted bitumen

Series	Range	Main component	‰*	Structure†
n-Alkanes	C_{13}–C_{35}	C_{23}	455	
Acyclic isoprenoids	C_{15}–C_{20}	C_{19}	75	
n-Alkylcyclohexanes	C_{13}–C_{28}		87	I
n-Alkylmethylcyclohexanes	C_{18}–C_{28}		87	II
Bicyclic terpanes	C_{14}–C_{16}	C_{16}	45	III, IV
Diterpanes	C_{19}–C_{20}		40	V, VI
Tricyclic terpanes	C_{19}–C_{28}	C_{23}	45	VII
Tetracyclic terpanes	C_{24}	C_{24}	10	VIII
Tetracyclic 17,21-secohopanes	C_{24}	C_{24}	10	IX
8,14-secohopanes	C_{27}–C_{30}		6	X
Ring-D aromatized 8,14-secohopanes	C_{27}–C_{31}	C_{29}	5	XI
Steranes	C_{27}–C_{29}		10	XII–XV
Pentacyclic hopanes	C_{27}–C_{35}	C_{30}	110	XVI–XVIII
Benzohopanes	C_{32}–C_{35}	C_{32}	10	XIX
Hexacyclic hopanes	C_{31}	C_{31}	5	XX

*Relative abundances in the saturated fraction.
†Roman numbers refer to the structures shown in Appendix 1.

ring system of the hopanoids. The land plant derived 4β(H)-eudesmane (IV) (Philp and Gilbert, 1988a) and a C_{14} nordrimane hydrocarbon were also detected in minor amounts.

Three compounds with MW 262 corresponding to C_{19}-tricyclanes were detected in the saturated fraction. The mass spectra of the two most prominent compounds corresponded to those reported by Philp (1985) for norabietane (V) and another isomer not yet identified. The third one is possibly a C_{19} tricyclic terpane. A C_{20} diterpenoid, abietane (VI), was also found in the extracts. Some aromatic diterpenoids, such as simonellite, tetrahydroretene and retene were also found in the aromatic fraction and have already been described (del Río *et al.*, 1993). Tricyclic diterpenoids are widespread in the plant kingdom, and are major constituents of conifer resins. Their presence in this sample therefore can be considered as an indication for the contribution of higher plant materials, mainly conifers, to the original organic matter (Philp and Gilbert, 1986b; Simoneit, 1986).

The partial *m/z* 191 mass fragmentogram (Fig. 6) shows the series of tricyclic terpenoid hydrocarbons (C_{19}–C_{28}, VII) detected in the saturation fraction of the POS. The predominant member of this series was the C_{23} homologue, whereas the C_{22} and C_{27} members were present in very low relative proportions, as expected, due to the unfavourable loss of methyl

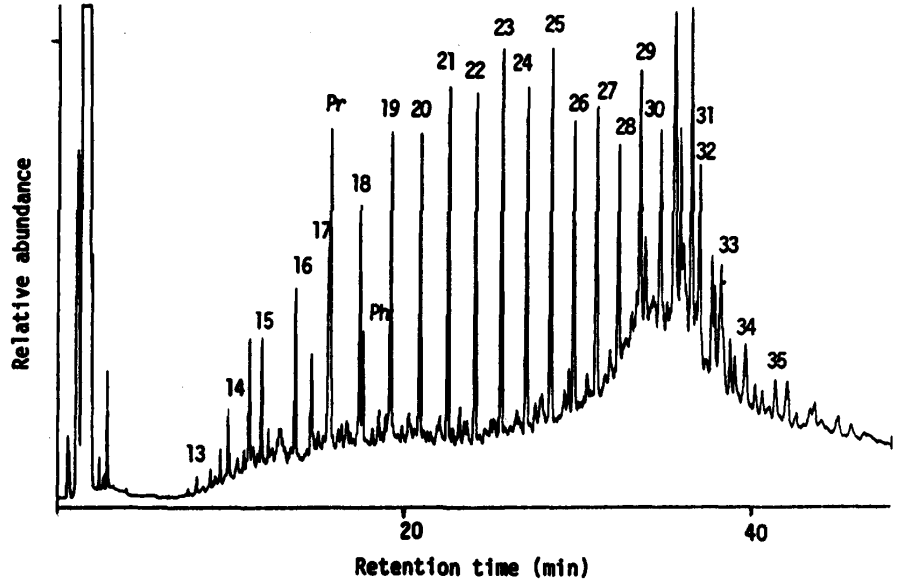

Fig. 3. Gas chromatogram (FID response) of the saturated fraction extracted from the Puertollano Oil Shale.

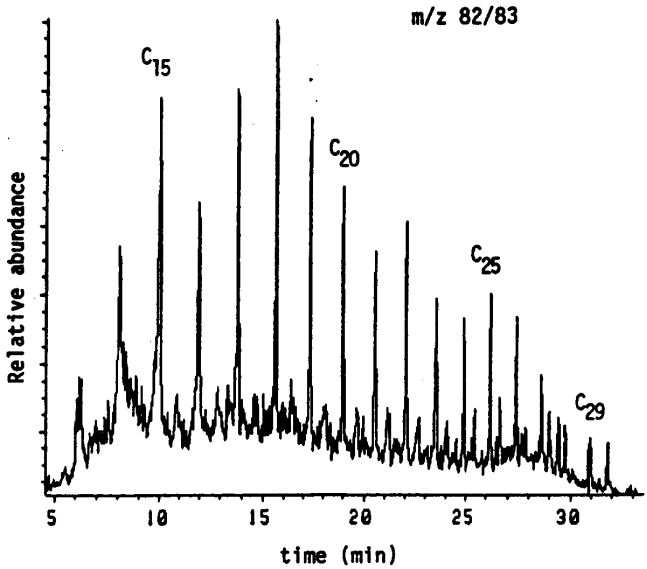

Fig. 4. m/z 82–83 Mass chromatogram showing the distribution of the n-alkylcyclohexane series.

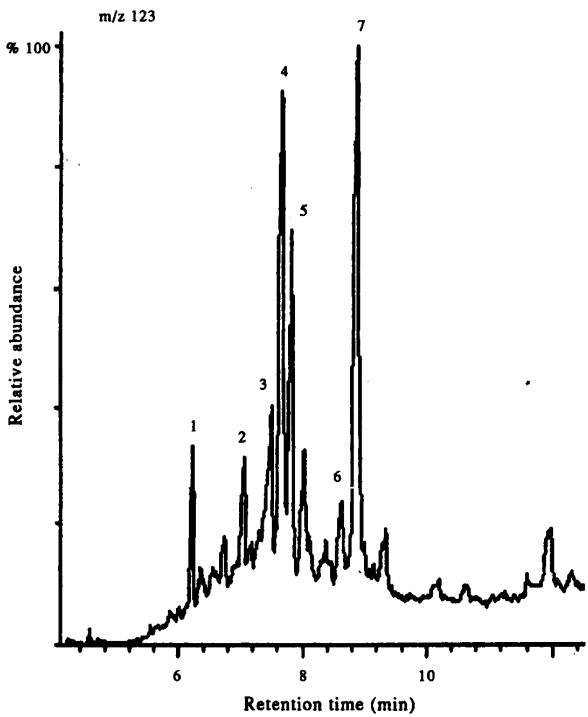

Fig. 5. Partial chromatogram of m/z 123 showing the presence of sesquiterpenoid hydrocarbons. For peak assignments refer to Table 3.

groups in positions C_{21} and C_{26} (Moldowan *et al.*, 1983). The C_{26} and C_{28} components were resolved as the R and S isomers. Different natural precursors such as tricyclohexaprenol, formed anaerobically from a ubiquitous cell constituent, hexaprenol, have been proposed as likely precursors for this series (Aquino Neto *et al.*, 1983; Moldowan *et al.*, 1983; Ekweozor and Strausz, 1983; Cyr and Strausz, 1983).

Two compounds with a molecular ion at m/z 330 and prominent fragments at m/z 191 were identified as C_{24} tetracyclanes (Fig. 6). According to their mass spectra, relative retention times and the assignments made by Aquino Neto *et al.* (1983) and Czochanska *et al.* (1988), the compound eluting between the C_{24} and C_{25} tricyclic terpanes was tentatively identified as a des-A triterpenoid hydrocarbon derived from either an oleanane (**VIII**, R1 = H, R2 = CH_3) or ursane (**VIII**, R1 = CH_3, R2 = H) skeleton. This compound is a degradation product of higher plant triterpenoids with oxygenated functional groups at the C-3 position of the skeleton e.g. α- and β-amyrin). The second compound has a retention time betweeen the C_{25} and C_{26} tricyclic terpanes and corresponds to a C_{24} 17(21)-secohopane (**IX**). The tetracyclic terpanes with a 17(21)-secohopane skeleton are usually present in the C_{24}–C_{27} range. (Aquino Neto *et al.*, 1983). The transformation of hopanoids into tetracyclic compounds is thought to occur by cleavage of the 17(21) bond of the pentacyclic hopanoids (see Fig. 7) either by microbial activity, during early diagenesis, or by thermocatalytic degradation (Trendel *et al.*, 1982). The presence of the C_{24} tetracyclanes has been reported previously in relatively high abundance in coals, and oils derived mainly from terrigenous source materials. In the POS, the high abundance of the C_{24} tetracyclanes, relative to the tricyclic terpanes, can be considered as an indication of a significant input of higher plant material (Trendel *et al.*, 1982).

A complex mixture of 8,14-secohopanes (**X**) was also detected in trace amounts in the saturated fraction of the POS. Due to the complexity, the series was analyzed by GC–MS/MS of the characteristic fragment ion m/z 123 and the corresponding molecular ions at m/z 372 + 14n as shown in Fig. 8. The series was detected in the C_{27}–C_{32} range, with the exception of the C_{28} homolog. Two stereoisomers (*S* and *R*) were detected for the C_{31} and C_{32} homologs. The presence of different isomers for each carbon number was also confirmed, although the assignment of their stereochemistry was not possible. 8(14)-secohopanes derive directly from hopanes by ring-C opening and might be the precursors of the series of bicyclic sesquiterpenoids with the drimane skeleton, discussed previously, by further cleavage of the 11(12) bond (Alexander *et al.*, 1984; Hussler *et al.*, 1984a), as shown in Fig. 7.

Ring-D aromatized 8,14-secohopanes (**XI**) have also been identified by monitoring the ion at m/z 365 as shown in Fig. 9. This series of compounds was found in the C_{29}–C_{32} range and was dominated by the C_{29} homolog, as observed in other sediments (Hussler *et al.*, 1984b; Connan *et al.*, 1986). It has been

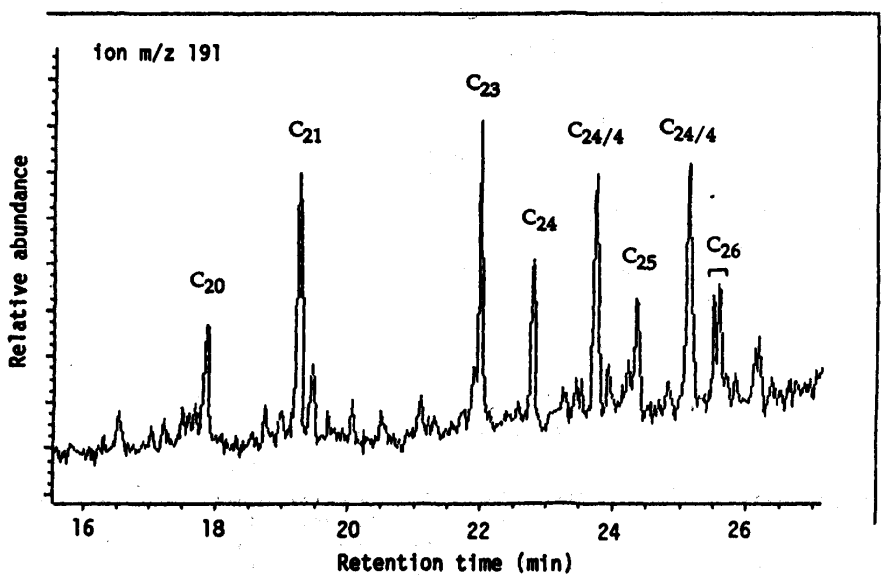

Fig. 6. Partial chromatogram of the ion at m/z 191 showing the tricyclic and tetracyclic terpenoid hydrocarbons.

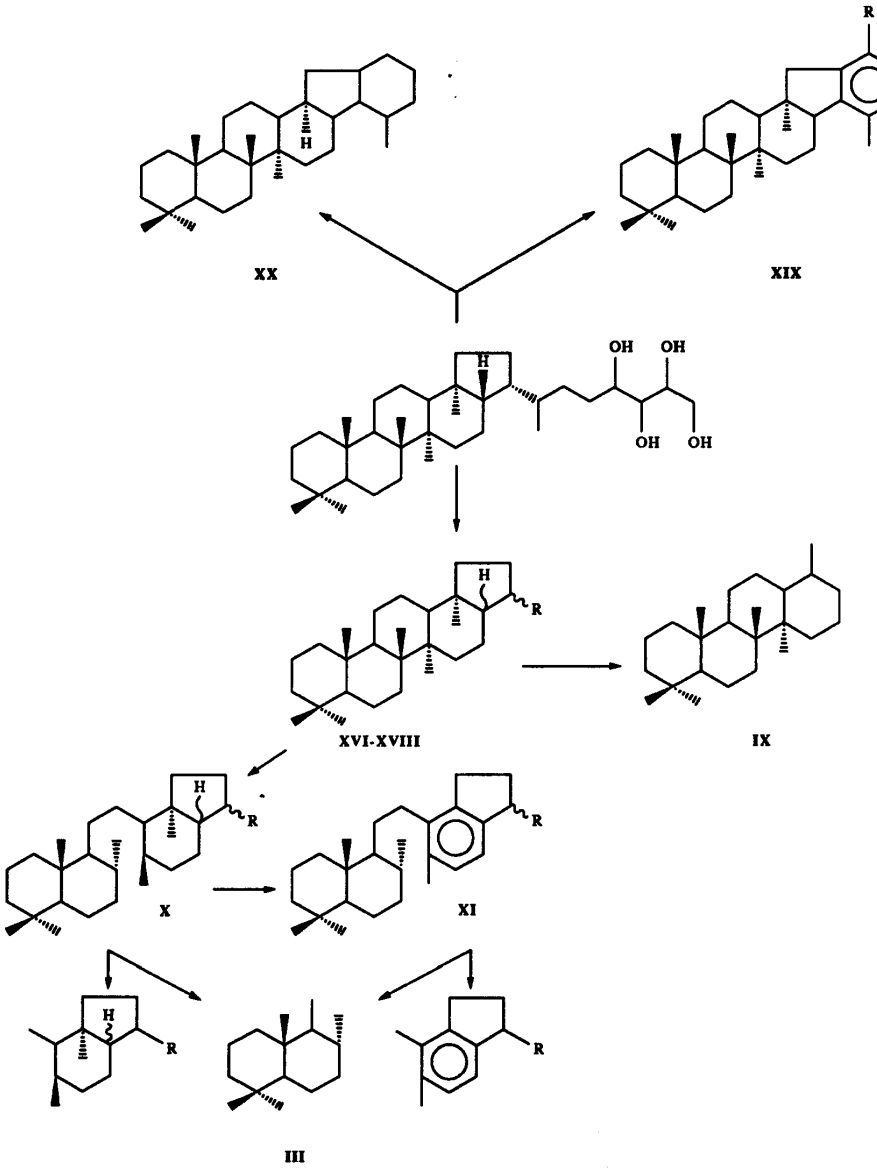

Fig. 7. Probable diagenetic pathway for the hopanoid compounds present in the Puertollano oil shale. Roman numbers refer to the structures showed in the Appendix.

proposed that this series is formed as consequence of thermal alteration of hopanoid precursors (Rinaldi *et al.*, 1988). These types of compounds have been detected in immature oil shales (Hussler *et al.*, 1981) and have been considered to indicate evaporite-carbonate environments. The monoaromatic secohopanes are formed by ring-C opening of a hopane precursor and subsequent aromatization (see Fig. 7).

The distribution of the penta- and hexacyclic hopanoid hydrocarbons (C_{27}–C_{35}) (**XVI–XX**) detected in the POS is shown in the m/z 191 mass fragmentogram (Fig. 10). Table 4 lists the identities of the individual components, according to previously reported mass spectra and relative retention times (Seifert and

Moldowan, 1978; Philp, 1985). The ubiquitous presence of hopanes in geological samples has been related to bacterial activity, and a contribution of green-blue algae (Ourisson *et al.*, 1979). In the POS extracts they consist mainly of the 22*S* and 22*R* 17α(H),21β(H)-hopanes at equilibrium concentrations for the extended homologues. The most abundant components are 17α(H),21β(H)-trisnorhopane (Tm) (B, **XVII** R = H), 17α(H),21β(H)-norhopane (C, **XVII**, R = C_2H_5) and 17α(H),21β(H)-hopane (E, **XVII**, R = *i*-C_3H_7). The series of 17β(H),21α(H)-moretanes (**XVIII**) is also present in lower proportion. The abundance of the C_{29} and C_{30} primary triterpanes, relative to the other members of the series, suggests that the oil shale has a low maturity level. The ratio of C_{30} 17β(H),21α(H)-moretane to 17α(H),21β(H)-hopane has also been used as parameter for maturity level, and its value in the Puertollano oil shale (0.37) also suggests that this sample has not attained maturity. The predominance of Tm over Ts also might indicate a moderate maturity level for this sample.

A series of compounds with molecular weights 432, 446, 460 and 474 and a base peak at *m/z* 191 was also observed in the partial chromatogram of the ion *m/z* 191 (Fig. 10). These compounds corresponds to a series of benzohopanes (**XIX**) ranging from C_{32} to C_{35} and previously reported by Hussler *et al.* (1984b) and Rinaldi *et al.* (1988). Hussler *et al.* (1984b) suggested that benzohopanes derive from bacteriohopanetetrol by dehydration and cyclization during very early diagenesis. Subsequent degradation of the side chain

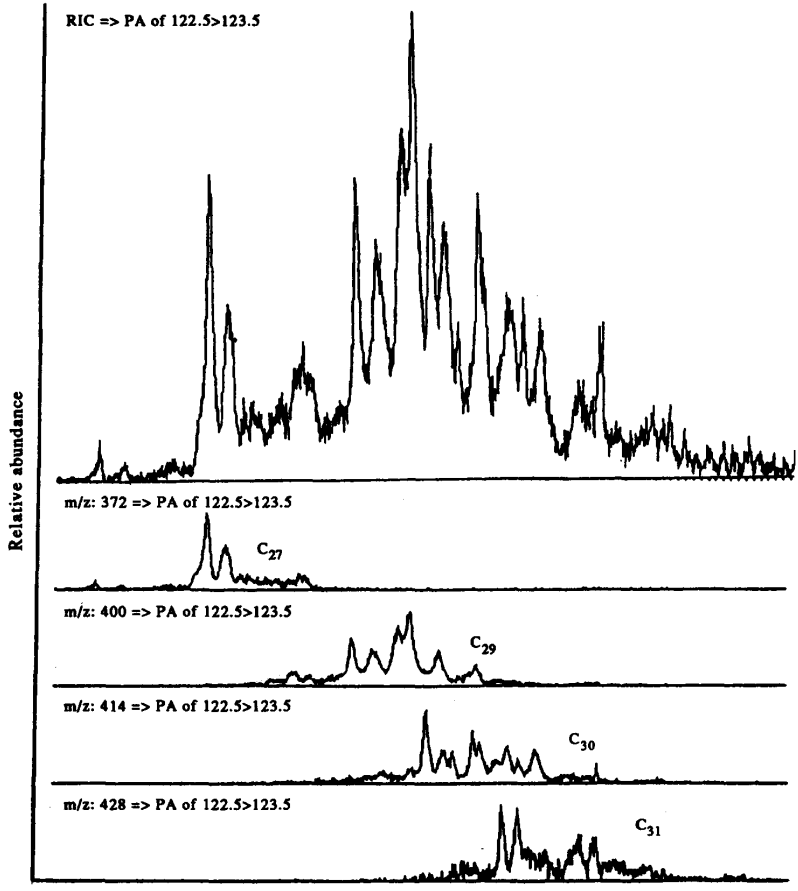

Fig. 8. Chromatograms of GC–MS/MS in parent mode (daughter ion at *m/z* 123) showing 8,14-secohopane distribution (parent ions at *m/z* 372, 400, 414 and 428).

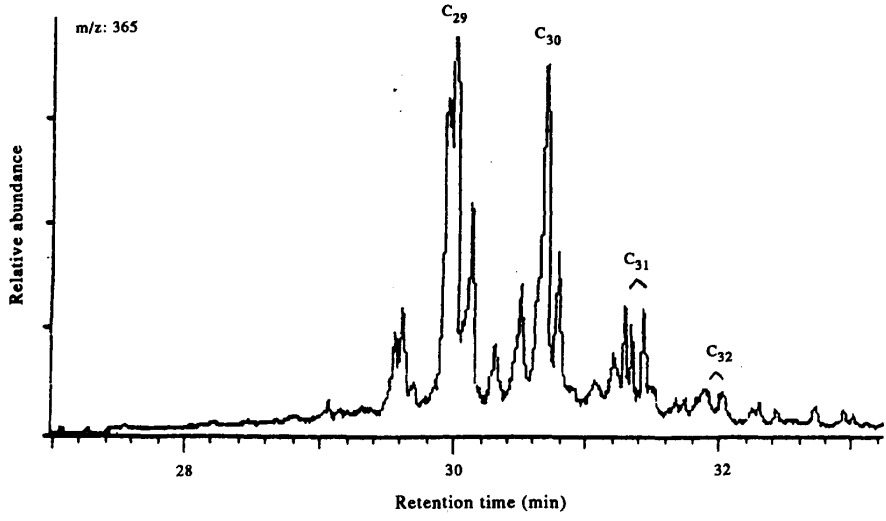

Fig. 9. Partial mass chromatogram of the ion at m/z 365 showing the ring-D monoaromatic 8,14-seco-hopane distribution.

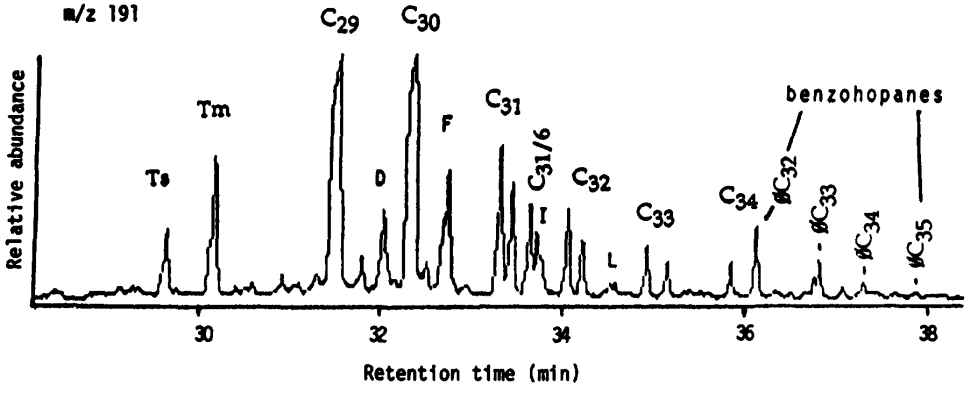

Fig. 10. Mass chromatogram of the ion at m/z 191 showing the penta- and hexacyclic triterpenoid distribution. C_{29}–C_{34} refer to the 17α,21β isomers; capital letters refer to the 17β,21α isomers listed in Table 4. $C_{31/6}$ is an hexacyclic hopanoid. ϕ_{32}–ϕC_{35} are the benzohopanes.

would lead to the formation of the lower homologs. On the other hand, Rinaldi *et al.* (1988) postulated biological oxidation before the degradation reaction to explain the formation of the lower members of the series. Aromatization might be carried out by bacterial oxidation under anaerobic conditions.

Table 3. Peak identifications for the m/z 123 mass chromatogram in Fig. 5

Peak No.	Identity	Formula	Structure
1	Nordrimane	$C_{14}H_{26}$	
2	Eudesmane	$C_{15}H_{28}$	IV
3	Rearranged drimane	$C_{15}H_{28}$	
4	8β-Drimane	$C_{15}H_{28}$	III R = CH_3
5	Desmethyl homodrimane	$C_{15}H_{28}$	
6	Isomer of homodrimane	$C_{16}H_{30}$	
7	8β-Homodrimane	$C_{16}H_{30}$	III R = C_2H_5

A compound with a retention time between the C_{31} and C_{32} 17α-hopanes, and a mass spectrum with a base peak at m/z 191 and molecular ion at m/z 424, was also detected. Its mass spectrum was similar to that reported by Rinaldi *et al.* (1988) and Connan and Dessort (1987) for a C_{31} hexacyclic hopane ($C_{31/6}$), the 18α(H)-hexacyclic hopane (**XX**). This compound is thought to be formed by cyclization of bacterihopanetetrol during the very early diagenetic process (see Fig. 7). The hexacyclic hopanoid series reported by Connan and Dessort (1987) in the C_{32}–C_{35} range was not detected in this oil shale,

Table 4. Peak identifications for m/z 191 mass chromatogram in Fig 10

Compound	Elemental composition	Structure
A 18α(H)-22,29,30-trisnorneohopane (Ts)	$C_{27}H_{46}$	XVI
B 17α(H)-22,29,30-trisnorhopane (Tm)	$C_{27}H_{46}$	XVII, R = H
C 17α(H),21β(H)-30-norhopane	$C_{29}H_{50}$	XVII, R = C_2H_5
D 17β(H),21α(H)-30-norhopane	$C_{29}H_{50}$	XVIII, R = C_2H_5
E 17α(H),21β(H)-hopane	$C_{30}H_{52}$	XVII, R = i-C_3H_7
F 17β(H),21α(H)-hopane	$C_{30}H_{52}$	XVIII, R = i-C_3H_7
G 17α(H),21β(H)-homohopane (22S)	$C_{31}H_{54}$	XVII, R = s-C_4H_9
H 17α(H),21β(H)-homohopane (22R)	$C_{31}H_{54}$	XVII, R = s-C_4H_9
I 17β(H),21α(H)-homohopane	$C_{31}H_{54}$	XVIII, R = s-C_4H_9
J 17α(H),21β(H)-bishomohopane (22S)	$C_{32}H_{56}$	XVII, R = s-C_5H_{11}
K 17α(H),21β(H)-bishomohopane (22R)	$C_{32}H_{56}$	XVII, R = s-C_5H_{11}
L 17β(H),21α(H)-bishomohopane	$C_{32}H_{56}$	XVIII, R = s-C_5C_{11}

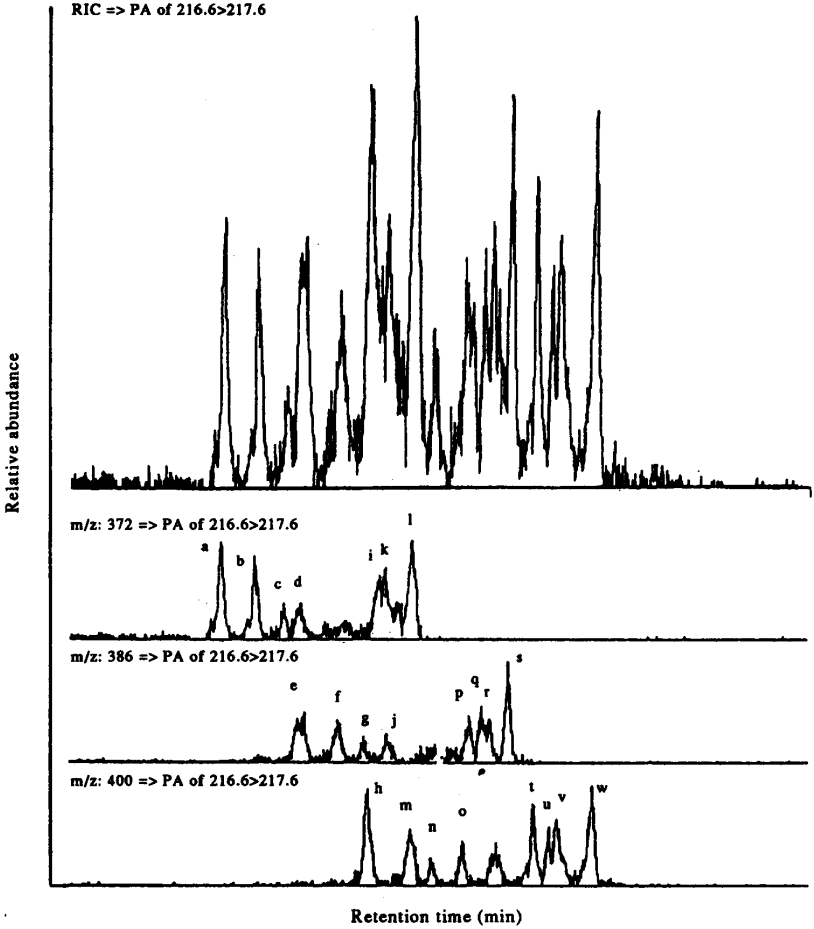

Fig. 11. Chromatograms of GC-MS/MS in parent mode (daughter ion at m/z 217) showing distributions of C_{27}, C_{28} and C_{29} steranes (parent ions at m/z 372, 386, 400). For peak assignments refer to Table 4.

suggesting that it has a different diagenetic route of formation than this $C_{31/6}$ compound.

The distribution of steranes in the saturated fraction of the POS consists of a complex mixture of regular and rearranged steranes in the C_{27}–C_{29} range and of which many coelute. In order to resolve this complex mixture, the steranes were analyzed by GC–MS/MS. The distribution of sterane parent ions (m/z 372, 386 and 400) of the daughter ion at m/z 217 for the Puertollano oil shale is given in Fig. 11,

Table 5. Peak identification for m/z 217 mass chromatogram in Fig. 11

Compound	Elemental composition	Structure
a 13β,17α-diacholestane (20S)	$C_{27}H_{48}$	**XIV**, R = H
b 13β,17α-diacholestane (20R)	$C_{27}H_{48}$	**XIV**, R = H
c 13α,17β-diacholestane (20S)	$C_{27}H_{48}$	**XV**, R = H
d 13α,17β-diacholestane (20R)	$C_{27}H_{48}$	**X**, R = H
e 13β,17α-24-methyldiacholestane (20S)	$C_{28}H_{50}$	**XIV**, R = CH_3
f 13β,17α-24-methyldiacholestane (20R)	$C_{28}H_{50}$	**XIV**, R = CH_3
g 13α,17β-24-methyldiacholestane (20S)	$C_{28}H_{50}$	**XV**, R = CH_3
h 13β,17α-24-ethyldiacholestane (20S)	$C_{29}H_{52}$	**XIV**, R = C_2H_5
i 14β,17β-cholestane (20R)	$C_{27}H_{48}$	**XIII**, R = H
j 14β,17β-cholestane (20S)	$C_{27}H_{48}$	**XIII**, R = H
k 13α,17β-24-methyldiacholestane (20R)	$C_{28}H_{50}$	**XV**, R = CH_3
l 14α,17α-cholestane (20R)	$C_{27}H_{48}$	**XII**, R = H
m 13β,17α-24-ethyldiacholestane (20R)	$C_{29}H_{52}$	**XIV**, R = C_2H_5
n 13α,17β-24-ethyldiacholestane (20S)	$C_{29}H_{52}$	**XV**, R = C_2H_5
o 13α,17β-24-ethyldiacholestane (20R)	$C_{29}H_{52}$	**XV**, R = C_2H_5
p 14α,17α-24-methylcholestane (20S)	$C_{28}H_{50}$	**XII**, R = CH_3
q 14β,17β-24-methylcholestane (20R)	$C_{28}H_{50}$	**XIII**, R = CH_3
r 14β,17β-24-methylcholestane (20S)	$C_{28}H_{50}$	**XIII**, R = CH_3
s 14α,17α-24-methylcholestane (20R)	$C_{28}H_{50}$	**XII**, R = CH_3
t 14α,17α-24-ethylcholestane (20S)	$C_{29}H_{52}$	**XII**, R = C_2H_5
u 14β,17β-24-ethylcholestane (20R)	$C_{29}H_{52}$	**XIII**, R = C_2H_5
v 14β,17β-24-ethylcholestane (20S)	$C_{29}H_{52}$	**XIII**, R = C_2H_5
W 14α,17α-24-ethylcholestane (20R)	$C_{29}H_{52}$	**XII**, R = C_2H_5

showing the total distribution of C_{27}–C_{29} steranes. The identities of the individual components are presented in Table 5. The data show a similar abundance of C_{27} (**XII**, R = H), (**XII**, R = CH_3) and C_{29} (**XII**,R = C_2H_5) pseudohomologues. The 5α(H),14α(H),17α(H) isomers (**XII**) predominated over the 5α(H),14β(H),17β(H) isomers (**XIII**), and a high abundance of diasteranes (**XIV**, **XV**) was also apparent. A 4-methyl C_{30} sterane appeared to be present by monitoring the parent/daughter ions at m/z 414 and 231, although no definite structure could be assigned for this compound. The predominance of the biologically occurring $\alpha\alpha$R isomers over the maturation induced $\beta\beta$ isomers is an indication of the low maturity level of this oil shale, and also of the absence of biodegradation (Philp, 1986).

CONCLUSIONS

The hydrocarbon distribution in the Puertollano oil shale is dominated by *n*-alkanes, *n*-alkylcyclohexanes, *n*-alkylmethylcyclohexanes and mid-chain monomethyl alkanes. Triterpenoid distributions in the hydrocarbon fraction of the Puertollano oil shale showed a major contribution of bacterially derived hopanoids. The compounds identified comprised the C_{27}–C_{35} hopanes (no C_{28}), C_{27}–C_{32} 8,14-secohopanes, C_{29}–C_{32} ring-D aromatized 8,14-secohopanes, C_{32}–C_{35} benzohopanes and a C_{31} hexacyclic saturated hopane. The gymnosperm and angiosperm derived material is evident in two different groups of diagenetic compounds. Diterpenoids compounds such as abietane, norabietane, simonellite, retene and the sesquiterpenoid cadalene are characteristics of the conifer resins, whereas the terpanes with oleanane and ursane skeleton are characteristics of angiosperms. It is concluded from the results that the Puertollano oil shale has been formed in a lacustrine environment with significant input of higher plant derived organic materials.

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APPENDIX

Structures Cited in Text